Economical low-light photovoltaics by using the Pt-free dye-sensitized solar cell with graphene dot/PEDOT:PSS counter electrodes

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Abstract
Graphene dots (GDs) are used for enhancing the performance of the poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS)-based counter electrodes in Pt-free dye-sensitized solar cells (DSSCs). As compared to PEDOT:PSS CEs, GD–PEDOT:PSS films possess a rough surface morphology, high conductivity and electrocatalytic activity, and low charge-transfer resistance toward I\(^{-}\)/I\(_{3}^{+}\) redox reaction, pushing cell efficiency to 7.36%, which is 43% higher than that of the cell with PEDOT:PSS CEs (5.14%). Without much impact on efficiency, the DSSCs with GD-PEDOT:PSS CEs work well under low-light conditions (light intensity <13.5 mW cm\(^{-2}\) and angle of incidence > 60\(^{\circ}\)), such as indoor and low-level outdoor lighting and of the sun while the other traditional cells would fail to work. The concurrent advantage in low cost in Pt-free materials, simple fabrication processes, comparable efficiency with Pt CEs, and high performance under low-light conditions makes the DSSC with GD-PEDOT:PSS CEs suitable to harvest light for a diverse range of indoor and low-level outdoor lighting locations.

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Introduction

For the practical use of solar cells, the light source usually does not match the ideal solar power density (100 mW cm$^{-2}$), and the angle of incidence (AOI) of the sun changes during the day and depends on the installation location. Moreover, a large number of diffused (scattered) light are created after sunlight passes through the atmosphere and reaches the earth; on cloudy days, over 90% of the light is diffused. It is well known that most common Si solar cells strongly depend on light incident angle [1-4]. Although incorporating the light tracing systems, it still exhibits poor performance under low-light condition, such as cloudy day, early morning and nightfall of a day [1]. Accordingly, it is important to develop the low-light solar cells which can achieve excellent conversion efficiency even in broadly diffused light and poor weather conditions. Moreover, the low-light solar cell enables new indoor applications such as smart home and intelligent building, with an average power consumption in the range of microwatts, including sensors, chargers, and standby power. For example, indoor light-emitting diode (LED) has been tremendous potential as supplemental lighting systems for crop production and low-light photovoltaics could be used to harvest the residual light energy, which is not absorbed by the crop.

In contrast with conventional Si solar cells, the performance of dye-sensitized solar cells (DSSCs) are less affected by the light intensity and less sensitive to the AOI [1,5], which makes DSSCs to be the most efficient photo-to-electron conversion devices under indoor and low-level outdoor lighting. A typical DSSC consists of a dye-sensitized mesoporous TiO$_2$ photoanode, an electrolyte containing tri-iodide/iodide (I$_3^-$/I$^-$) redox couple and a counter electrode (CE). The CE, a crucial part in a DSSC, should possess a good conductivity for the transportation of electrons flowing through an external circuit and a superior catalytic ability for the reduction of I$_3^-$ for reducing the energy loss caused by the charge transfer overpotential between the electrolyte and the CEs [6-8]. In DSSCs, Pt is the most used catalyst on the CE because of its high conductivity, stability and high electrocatalytic activity toward I$_3^-$/I$^-$ redox reaction. However, the high cost and energy-consuming fabrication process of the Pt CE limits its applicability. By replacing Pt with other cheaper electrocatalytic materials, the cost of fabrication of DSSCs on industrial scale can be greatly reduced, that would heighten the competitiveness of DSSCs in solar cell markets. Recently, conducting polymers (such as poly(3,4-ethylene dioxythiophene) (PEDOT) [9], poly(3,3-diethyl-3,4-dihydro-2H-thieno-[3,4-b][1,4]-dioxepine) (PProDOT-Et$_2$) [10], polypyrrole (PPy) [11], and polyaniline (PANI) [12]) and carbonaceous materials (such as carbon black (CB) [13], graphite [14], carbon nanotube (CNT) [15], and graphene [16]) have become the most promising candidates as catalysts of CE for DSSCs because they are metal element-free, abundant and low cost, and possess good electrocatalytic activity.

A water-dispersible conducting polymer, poly(3,4-ethylene dioxythiophene):poly(4-styrene sulfonate) (PEDOT:PSS), has attracted much attention as the catalytic CEs of DSSCs mainly due to its exceptional advantage of aqueous solution processibility [17]. However, pristine PEDOT:PSS films are plagued by a low conductivity (generally below 1.5 cm$^{-1}$) and poor electrocatalytic activity for the reduction of I$_3^-$ (unobvious cathodic peak current density) due to the nonconductive counter anion, PSS$^-$, disturbing the conduction path of PEDOT inside the film as well as the poor catalytic surface area of its flat film [17,18]. Inert solvents [19] or carbon materials [20-24] have been employed to improve conductivity and catalytic surface areas of PEDOT:PSS films. For example, by introducing CB into the PEDOT:PSS-based CEs for their DSSCs, $\eta$ can achieve to 7.01% [22]. Multiwall CNT-PEDOT:PSS composite CE for DSSCs exhibits $\eta$ of 6.50% [23]. A catalytic film composed of graphene and PEDOT:PSS for the use of CE in a DSSC had reached 4.50% efficiency [24]. However, a perfect graphene sheet usually possesses limited active sites for electrocatalytic reaction in spite of its extraordinarily high electrical conductivity [25].

Several strategies are employed to increase the electrocatalytic active sites on graphene sheets, such as chemical functionalization (e.g., oxygen-containing functional groups reduced graphene oxide) [26], heteroatom doping (e.g., nitrogen-doped graphene) [25,27,28], and nano-sized graphene pieces (e.g., graphene dots (GDs)). Among these graphene nanostructures, GDs have attracted great attention and been widely applied in bio-imaging [29-31], LEDs [32,33] and photovoltaics [34-37] due to their unique properties of quantum confinement and edge effects [34,38]. Moreover, nanometer-size and rich oxygen-containing group of GDs facilitate them to be well dispersed in common solvents [39], which is expected to enable various solution-processable applications.

In this study, the water-soluble GDs via microwave-assisted hydrothermal technique is incorporated into the PEDOT:PSS-based CEs for Pt-free DSSCs achieve an excellent $\eta$ of 7.36% under 1 sun AM 1.5 G, which to the best of our knowledge is the highest ever reported for a DSSC with PEDOT:PSS-based CEs. DSSCs with GD-PEDOT:PSS CEs can maintain the performance under various low-light conditions (light intensity <13.5 mWcm$^{-2}$ and angle of incidence >60°), such as white-light LEDs, noon of a cloudy day, and early morning and nightfall of a sunny day, as compared with conventional Si solar cells. Meanwhile, the DSSCs with GD-PEDOT:PSS CEs and with Pt CEs exhibit similar $\eta$ under low-light conditions. Less performance degradation of DSSCs under low-light, compared with the Si solar cells, is due to reduced $J_{sc}$ degradation and improved $FF$. The concurrent advantage in low-cost materials, simple fabrication processes and high performance under low light make our Pt-free DSSCs playing a crucial role in energy-harvesting systems for smart-home and intelligent buildings.

Experimental

Materials

Lithium iodide (LiI, synthetical grade) and iodine (I$_2$, synthetical grade) were obtained from Merck. Acetone (99+%), Tert-butyl alcohol (tBA, 96%), guanidine thiocyanate (GuSCN, 99+%), and 4-tert-butylpyridine (TBP, 96%) were bought from Acros. Ti (IV) tetraisopropoxide (TTIP, >98%), lithium perchlorate (LiClO$_4$, ≥98.0%), ethanol (EtOH, absolute), isopropyl alcohol (IPA, 99.5%), and 2-methoxyethanol (99.95%), were

Materials
received from Sigma-Aldrich. Acetonitrile (ACN, 99.99%) was procured from J. T. Baker. 1,2-dimethyl-3-propylimidazolium iodide (DMPII) and cis-diso-oxycyanato-bis-(2,2’-bipyridyl-4,4’-dicarboxylato) ruthenium (II) bis(tetra-butylammonium) (N719 dye) were purchased from Solaronix (S.A., Aubonne, Switzerland). PEDOT: PSS aqueous solution (PH 500, 1.0-1.4 wt% dispersion in water) was obtained from Heraeus.

**Synthesis of water soluble GDs solution**

The GD solution was prepared by using glucose and deionized-water as the source and solvent, respectively [33]. First, 2.5 mL glucose solutions were transferred to a glass bottle with 4 mL volume and a tightened cover. The glass bottle was then heated with a microwave oven at a power of 595 W for 9 min. Subsequently, the GD solution was cooled to room temperature, and the water soluble GDs solution was thus prepared. The GD sample was dialyzed by molecular weight cutoff (MWCO) of 1000 against DI water for characterization. The yield of the GDs was determined to be around ~80%. As we do not know how many glucose molecules were converted to GDs, thus the concentration of GDs could not be determined.

**Preparation of CEs**

The fluorine-doped SnO₂ (FTO, TEC-7, 10 Ω sq⁻¹, NSG America Inc., New Jersey, USA) conducting glasses were first cleaned with a neutral cleaner and then washed with DI-water, acetone, and IPA sequentially. The standard Pt CE was prepared by sputtering for 5 nm of Pt on the cleaned FTO substrate. The PEDOT: PSS film was prepared with a mixing solution composed of 50 V% PEDOT: PSS aqueous solution and 50 V% ethanol. For the GDs-PEDOT: PSS mixing solution, the GD solution content in the above mixing solution (PEDOT:PSS, GDs, and ethanol solution) was optimized by applying different volume ratios from 10 V% to 40 V% as shown in Figure S1 (see Supporting information). The optimized ratio was found to be 30 V% GD solution content. Therefore, another mixing solution composed of 50 V% PEDOT: PSS aqueous solution, 30 V% GDs solution, and 20 V% ethanol was used for preparing the GDs-PEDOT: PSS composite film. These films were fabricated on the cleaned FTO substrates via drop-coating method and then heated to 60 °C for 30 min.

**Fabrication of DSSCs**

The conducting surface of the FTO was treated with a solution of TTIP in 2-methoxyethanol (weight ratio of 1:3) for obtaining a good contact between the conducting glass and the TiO₂ film. For the mesoporous double-layer TiO₂ film, 12-μm-thick transparent layer (diameter of 20-50 nm, Eversolar P-300) and 5-μm-thick (light-scattering layer (PST-400, JGC Catalysts and Chemicals, Japan) were deposited on the treated FTO sequentially by a conventional screen-printing method. A portion of 0.4 x 0.4 cm² was selected from the double-layer TiO₂ film as the active area by removing the side portions by scraping. The TiO₂ film was gradually heated to 500 °C in an oxygen atmosphere and subsequently sintered at 500 °C for 30 min. After sintering at 500 °C and cooling to 80 °C, the TiO₂ electrode was immersed in a 3 x 10⁻⁴ M N719 dye solution with a mixed solvent of ACN/tBA (volume ratio of 1/1) at room temperature for 24 h. Such a prepared TiO₂ electrode was coupled with a CE; these two electrodes were separated by a 25 μm-thick Surlyn® film (SX1170-25, Solaronix S.A., Aubonne, Switzerland) and sealed by heating. A mixture of 1.2 M DMPII, 0.35 M I₂, 0.1 M GdSCN, and 0.5 M TBP in ACN/MPN (volume ratio of 8/2) was used as the electrolyte. The electrolyte was injected into the gap between the two electrodes by capillarity.

**Measurements and instruments**

Transmission electron microscopy (TEM, JEM-2100F, JEOL) was performed at operating voltage of 200 kV. The height of the GDs was characterized by atomic force microscope (AFM, NanoScope IV, Digital Instruments) under tapping mode. UV-visible spectrum was obtained for the GD solution by using an UV-Visible spectrophotometer (UV-VIS-NIR, V670, Jasco Co., Japan). For characterization of photoluminescence (PL) spectra, the excitation and emission spectra of the GD solution were recorded using an FLS920P Edinburgh Analytical Instrument apparatus with Xe lamp as an excitation source. The surface morphologies of various catalytic films were observed by field emission scanning electron microscopy (FE-SEM, Nova Nano-SEM 230, FEI, Oregon, USA).

The surface of the DSSC was covered by a mask leaving a light-illuminating area of 0.16 cm², and then illuminated by a class - A quality solar simulator (XES-3015S, AM 1.5G, SANG-EL ELECTRIC CO., LTD.). Incident light intensity (100 mW cm⁻²) was calibrated with a standard Si cell (PECST01, Peccell Technologies, Inc., Yokohama, Japan). Photoelectrochemical characteristics of the DSSC were recorded with a potentiostat/galvanostat (PGSTAT 30, Autolab, Eco-Chemie, the Netherlands). Electrochemical impedance spectroscopy (EIS) analysis was performed using the above-mentioned potentiostat/galvanostat, equipped with an FRA2 module. Herein, a symmetric sandwich-type cell was used to investigate the electrocatalytic ability of the CE by EIS with a frequency range from 10 mHz to 100 kHz; the symmetric cell consisting of an electrolyte and two identical electrodes with an area of 1 cm², separated by a Surlyn® film of 60 μm in thickness. Impedance spectra data were analyzed by fitting them to an equivalent circuit model [40,41], using Z-view software. Cyclic voltammetry (CV) was performed to investigate electrocatalytic abilities of the CEs. The CV was carried out with a three-electrode electrochemical system, by using an electrode with PEDOT or GDs-PEDOT: PSS or sputtered Pt catalytic film as the working electrode, a Pt foil as the CE, and an Ag/Ag⁺ electrode as the reference electrode in an ACN solution, containing 10 mM I⁻, 1 mM I₂, and 0.1 M LiClO₄.

**Results and discussions**

GDs are edge-bound nano-sized graphene pieces and exhibit unique electronic and optical properties due to the quantum confinement and edge effects [34,38]. The synthesized GDs were investigated by TEM, UV-visible spectroscopy, and PL.
spectroscopy. Figure 1a shows the TEM image of the monodispersed GDs, which exhibit uniform diameters of ~3.50 nm. As shown in the inset of Figure 1a, the HRTEM image indicates high crystallinity of GDs with a lattice parameter of 0.246 nm corresponding to the (1120) lattice fringes of graphene. Figure 1b shows the AFM image of the monodispersed GDs,

Figure 1 (a) TEM image of GDs and its corresponding HRTEM image (inset). (b) AFM image of the GDs and its corresponding height profile. (c) Absorbance spectrum of the GDs. (d) PL spectra of GDs. The inset in (d) shows photographs of the GDs solutions irradiated by ambient light (left) and UV light (right).

Figure 2 Cross-sectional SEM images of (a) PEDOT:PSS and (b) GD-PEDOT:PSS films. Corresponding top-view SEM images of (c) PEDOT:PSS and (d) GD-PEDOT:PSS films.
three GDs are selected randomly and labeled as A, B, and C. The average height of these GDs is 2.90 nm as shown in the inset of Figure 1b. As shown in Figure 1c, two absorption peaks at 228 and 282 nm are observed for the diluted GD solution, which consists with the result in the previous literature [33]. Figure 1d shows the PL spectra of the GD solutions. A broad emission peak at 450 nm is observed when the sample is excited by 300 nm. When the excitation wavelength changed from 300 to 500 nm, the PL peak shifts from 450 to 537 nm, and shows the decrease of PL intensity. The excitation wavelength-dependent emission wavelength and intensity observed here is a common phenomenon in carbon-based quantum dots [31,33]. Insets of Figure 1d are the photographs of GD solution taken under visible (left) and UV (right) light illumination, showing the excitation wavelength-dependent fluorescence of GDs.

Figure 2 shows SEM images of PEDOT:PSS and GD-PEDOT:PSS composite films on the FTO substrate. As shown in Figures 2a and b, the cross-sectional SEM image reveals that both PEDOT:PSS and GD-PEDOT:PSS composite films possess the similar film thickness of ~6.3 μm. It is observed from Figure 2b that the PEDOT:PSS film has flat surfaces with smooth morphology, which implies the unfavorable electrochemical surface area for the redox reaction. On the other hand, a rough surface morphology consisting of irregular island-like structures can be seen in the GD-PEDOT:PSS film, as shown in Figure 2c. The catalytic film with the high superficial roughness is expected to enhance its electrocatalytic activity for I₀⁻/I₃⁺ redox couple, as well as reduce the charge-transfer resistance at the interface of CE/electrolyte [7,37]. Moreover, we measured the sheet resistance of the PEDOT:PSS film with and without GDs and found that the GD-PEDOT:PSS film (1.5 × 10⁻⁴ Ω cm) possesses lower sheet resistance than the PEDOT:PSS film (9.6 × 10⁻⁴ Ω cm). Therefore, the attractive performance of the GD-PEDOT:PSS film as a CE in a DSSC can be excepted due to the large surface roughness and the improved conductivity.

Photocurrent density-voltage (J-V) characteristics of the DSSCs with PEDOT:PSS CEs and GD-PEDOT:PSS CEs are shown in Figure 3a, and the corresponding photovoltaic parameters are listed in Table 1. The cell with GD-PEDOT:PSS CEs shows the best performance with a cell efficiency (η) of 7.36%, an open-circuit voltage (VOC) of 718 mV, a fill factor (FF) of 0.70, and a short-circuit current density (JSC) of 14.70 mA cm⁻²; this η is much higher than that of the cell with PEDOT:PSS CE (5.14%). The Voc of the DSSC with GD-PEDOT:PSS CE (7.36%) is close to that of the cell with sputtered Pt CE (8.46%), as shown in Figure S2 in Supporting information. The surface morphology of the sputtered Pt CE is also shown in Figure S2 in Supporting information. It can be observed that Pt nanoparticles are uniformly distributed on the FTO substrate and the effective catalytic area of the Pt CE is mainly determined by the roughness of FTO layers. The high efficiency of the DSSC with GD-PEDOT:PSS CEs is due to its high JSC and FF, with references to that of the cell with PEDOT:PSS CEs. High JSC of the DSSC with GD-PEDOT:PSS CE may be attributed to more active electrocatalytic sites on rough catalytic GD-PEDOT:PSS films for reducing triiodide (I₃⁻) ions, compared to that in the flat PEDOT:PSS films. A faster movement of the redox couple is expected in the electrolyte of the DSSC with GD-PEDOT:PSS CEs due to the fast reduction of I₃⁻ ions at the CE of the cell, which in turn can lead to fast electron transfer kinetics in the cell and to a high FF for the cell (0.70), compared to that of the cell with PEDOT:PSS CE (0.60). These mechanisms will be discussed and verified later through CV and EIS.

Herein, the CV analysis was performed to understand the reaction kinetics and electrocatalytic activities of the CEs with PEDOT:PSS and GD-PEDOT:PSS for I₀⁻/I₃⁺ redox reaction by using a three-electrode electrochemical system. Figure 3b...
displays the CV curves of the electrodes with PEDOT:PSS and GD-PEDOT:PSS. Table 2 lists the corresponding cathodic current density. The electrode with GD-PEDOT:PSS shows a higher cathodic current density (−1.58 mA cm⁻²), corresponding to the reduction reaction of I₃⁻ ion at the interface of PEDOT:PSS with the electrolyte. We performed EIS analysis with symmetric sandwich-type cells having two identical electrodes. Figure 3c shows Nyquist plots of the symmetric sandwich-type cells with PEDOT:PSS electrodes, and the equivalent circuit is shown in the inset of Figure 3c. An EIS of a symmetric sandwich-type cell can be divided into two parts. The first semicircle in the high frequency range (10⁻⁵ Hz) represents the charge transfer resistance (Rct) at the electrode/electrolyte interface. The second semicircle in the low frequency range (0.1-10 Hz) represents the Warburg diffusion resistance (Rw) within the electrolyte. The Rct values of the symmetric sandwich-type cells with PEDOT:PSS electrodes are listed in Table 2. The symmetric sandwich-type cells with PEDOT:PSS electrodes possess Rct values of 10.38 and 7.92 Ω, respectively. A lower Rct value is observed for the symmetric sandwich-type cell with GD-PEDOT:PSS electrodes due to its higher electrocatalytic activity for the reduction of I₃⁻ ions. This result shows that PEDOT:PSS catalytic films can effectively catalyze the reduction of I₃⁻ ions to I⁻ ions due to low charge transfer resistance at the electrode/electrolyte interface, leading to the high performance of the DSSC with GD-PEDOT:PSS CEs.

In order to further investigate the charge transfer resistances (Rct) for the reduction of I₃⁻ ions at the interfaces of PEDOT:PSS and GD-PEDOT:PSS with the electrolyte, we performed EIS analysis with symmetric sandwich-type cells having two identical electrodes. Figure 3c shows Nyquist plots of the symmetric sandwich-type cells with PEDOT:PSS and GD-PEDOT:PSS electrodes, and the equivalent circuit is shown in the inset of Figure 3c. An EIS of a symmetric sandwich-type cell can be divided into two parts. The first semicircle in the high frequency range (10⁻⁵ Hz) represents the Rct at the electrode/electrolyte interface. The second semicircle in the low frequency range (0.1-10 Hz) represents the Warburg diffusion resistance (Rw) within the electrolyte. The Rct values of the symmetric sandwich-type cells with PEDOT:PSS and GD-PEDOT:PSS electrodes are listed in Table 2. The symmetric sandwich-type cells with PEDOT:PSS and GD-PEDOT:PSS electrodes possess Rct values of 10.38 and 7.92 Ω, respectively. A lower Rct value is observed for the symmetric sandwich-type cell with GD-PEDOT:PSS electrodes due to its higher electrocatalytic activity for the reduction of I₃⁻ ions. This result shows that PEDOT:PSS catalytic films can effectively catalyze the reduction of I₃⁻ ions to I⁻ ions due to low charge transfer resistances at the electrode/electrolyte interface, leading to the high performance of the DSSC with GD-PEDOT:PSS CEs.

In literatures, almost all of photovoltaics (PVs) characterizations were discussed with normal incident light. However, the conversion of light into electric energy occurring at low-light (in the fog or on overcast days, for example) should be considered for practical PV applications. Additionally, in real life, the AOI of sun light is always changed by time and depends on the installation location. Therefore, illumination intensity dependence of cell efficiency, incident angle dependence of cell

Table 2 Electrochemical parameters for different counter electrodes.

<table>
<thead>
<tr>
<th>CE with</th>
<th>Cathodic current density (mA cm⁻²)</th>
<th>ΔE_p (mV)</th>
<th>Rct (ohm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEDOT:PSS</td>
<td>-0.39</td>
<td>436</td>
<td>10.38</td>
</tr>
<tr>
<td>GD-PEDOT:PSS</td>
<td>-1.58</td>
<td>347</td>
<td>7.92</td>
</tr>
</tbody>
</table>

The values are obtained from CV; bThe values are obtained from EIS.

Figure 4 (a) Illumination intensity dependence of cell efficiency for various solar cells; the corresponding normalized data are shown in (b). (c) Incident angle dependence of cell efficiency for various solar cells; a schematic of incident angle dependent measurement is also shown in the figure as an inset; the corresponding normalized data are shown in (d).
Moreover, all of their photovoltaic parameters are shown in Figure 4a, our DSSCs show better performance than the Si solar cells. The corresponding normalized data are shown in Figure 4b and d, respectively.

The real-world case with weak light and large AOI conditions for the fabricated DSSCs are investigated and the correspond-...
conversion device at large AOs or under low-light irradiation, the cost-effective GD-PEDOT:PSS CEs, as compared to expensive Pt CEs, pave the way for commercializing DSSCs and thus heighten the competitiveness of DSSCs in solar cell markets.

4. Conclusions

The GD-PEDOT:PSS film with a rough surface, high electron conductivity, excellent electrocatalytic activity and low charge-transfer resistance toward I–/I3 redox achieves a η up to 7.36%, which is much higher than that of cell with pristine PEDOT:PSS CE (5.14%) and is close to that of cell with Pt CE (8.46%). The DSSCs with The GD-PEDOT:PSS CEs show superior performance under low-light conditions (light intensity <13.5 mW cm−2 and AOI > 60°), as compared with conventional Si solar cell. This study indicates that GD-PEDOT:PSS as an Pt-free CE for DSSCs paves the way for efficient light-harvesting devices for intelligent building and smart home.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2015.10.008.

References

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